

**RHEOLOGICAL PROPERTIES OF MOLTEN KILAUEA IKI
BASALT CONTAINING SUSPENDED CRYSTALS**

H. C. Weed
F. J. Ryerson
A. J. Piwinski

This paper was prepared for submittal to
American Chemical Society Monograph

February 1985

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

VAULT REFERENCE COPY

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

RHEOLOGICAL PROPERTIES OF MOLTEN KILAUEA IKI BASALT CONTAINING SUSPENDED CRYSTALS

H. C. Weed, F. J. Ryerson, and A. J. Piwinski

University of California, Lawrence Livermore National Laboratory
Livermore, CA 94550

ABSTRACT

In order to model the flow behavior of molten silicate suspensions such as magmas and slags, the rheological behavior must be known as a function of the concentration of suspended crystals, bulk composition, and external conditions. We have determined the viscosity and crystallization sequence for a Kilauea Iki basalt between 1250°C and 1150°C at 100 kPa total pressure and fO_2 corresponding to the quartz-fayalite-magnetite buffer in an iron-saturated Pt30Rh rotating cup viscometer of the Couette type. The apparent viscosity varies from 9 to 878 Pa.s. The concentration of suspended crystals varies from 18 volume percent. at 1250°C to 59 volume percent. at 1150°C. The molten silicate suspension shows power-law behavior: $\log \tau_{yx} = A_0 + A_1 \log |du/dx|$, where τ_{yx} is the shear stress and du/dx the shear rate. Since $A_1 \leq 1$, the apparent viscosity decreases with increasing shear rate and the system is pseudoplastic.

INTRODUCTION

In order to understand the flow behavior of molten silicates containing suspended crystals, we need to know the rheological properties of the system as a function of volume fraction of the suspended crystalline phases at appropriate temperatures, oxygen fugacities and bulk compositions. Because of the widespread occurrence of silicates, this approach can be applied to magma transport during volcanic eruptions, large scale convective and mixing processes in magmatic systems, and fouling of internal boiler surfaces by coal ash slags in plants burning pulverized coal.

EXPERIMENTAL METHODS

We are currently determining the dynamic viscosity and crystallization sequence for a basalt from Kilauea Iki, Hawaii at 100 kPa total pressure. Viscosities are being measured in an iron-saturated, Pt-30% Rh, rotating-cup viscometer of the Couette type from 1250° to 1150°C. The temperature interval for the crystallization sequence ranges from 1270° to 1130°C. Oxygen fugacity corresponding to the high temperature extrapolation of quartz-fayalite-magnetite buffer (i.e. QFM, see Huebner (1)) is maintained by flowing CO/CO₂ mixtures. In the crystallization sequence experiments, oxygen fugacity is monitored by a ZrO₂ sensor cell. Low temperature limits on the investigated crystallization sequence are dictated by the sluggish kinetics encountered in this system.

RESULTS

The major element bulk composition of the starting material used in our experiments is given in Table 1.

TABLE 1. Analyses of Starting Material

Oxide	Kilauea Iki	Shaw <u>et. al</u> (2)
SiO ₂	46.29	50.14
Al ₂ O ₃	10.44	13.37
MgO	17.90	8.20
FeO*	11.34	10.13
Fe ₂ O ₃	-	1.21
CaO	8.49	10.80
Na ₂ O	1.84	2.32
P ₂ O ₅	0.22	0.27
K ₂ O	0.40	0.53
TiO ₂	1.89	2.63
MnO	0.19	0.17
TOTAL	99.90	99.77

*All iron as FeO

The crystallization experiments were carried out employing a specimen of Kilauea Iki whole rock powder. The experimental results obtained at the QFM buffer are listed in Table 2. Olivine and chrome spinel are the only crystalline phases which occur between 1240° and 1179°C; clinopyroxene and plagioclase feldspar crystallize at approximately 1170°C. The concentration of crystals increases from about 22 weight percent. to about 28 weight percent. between 1250° and 1180°C. The liquid line of descent is characterized by a slight SiO₂, Al₂O₃ and alkali enrichment and an FeO and MgO depletion.

The volume percentage of melt as a function of temperature is shown in Figure 1. The break in slope at approximately 1170°C corresponds to the appearance of clinopyroxene and plagioclase feldspar (see Table 2).

TABLE 2. Results of Selected Kilauea Iki Liquidus Experiments

Exp't No.	Time (Hrs)	Temp (°C)	Experiment Products	Vol % Melt ^a	Wt % Melt ^b
14	93.0	1240	olivine, chrome spinel, glass	71.8	78.1
9	189.5	1230	olivine, chrome spinel, glass	80.2 ^c	76.1
8	24.0	1219	olivine, chrome spinel, glass	77.3	74.8
10	290.0	1209	olivine, chrome spinel, glass	76.2	74.2
12	289.0	1189	olivine, chrome spinel, glass	63.8	72.5
13	364.0	1179	olivine, chrome spinel, glass	71.8	71.5
16	380.0	1170	olivine, chrome spinel, clino-pyroxene, plagioclase, glass	69.6	68.5
19	400.0	1160	olivine, chrome spinel, clino-pyroxene, plagioclase, glass	54.7	53.5
20	400.0	1149	olivine, chrome spinel, clino-pyroxene, plagioclase, glass	40.7	49.8

a) Volume percent of melt was determined by a 1000 point mode on metallograph.

b) Weight percent of melt was determined by constrained least squares analysis of phase compositions.

c) Volume percent glass was determined by a 850 point mode on metallograph.

The volume percentage of melt, V_m , is given by Equations 1 and 2:

$$V_m (Ol+Chsp) = 0.157 T(^{\circ}C) - 114.0, \text{ where } T(^{\circ}C) \geq 1170, \quad 1)$$

$$V_m (Ol+Chsp+Cpx+Plag) = 1.36 T(^{\circ}C) - 1522.7, \text{ where } T(^{\circ}C) \leq 1170. \quad 2)$$

Extrapolation of Equation 1 to $V_m = 100$ corresponds to $T = 1360^\circ\text{C}$ for the liquidus. Extrapolation of Equation 2 to $V_m = 0$ yields $T = 1119^\circ\text{C}$ for the disappearance of liquid, the solidus temperature.

The measured apparent viscosities of the Kilauea Iki molten basalt between 1250° and 1150°C varied from 9 to 878 Pa·s. Sigmoidal torque versus rotation speed curves were obtained at all investigated temperatures. The curves are linear at rotation speeds less than 0.4 revolutions/second, with a positive slope. At higher rotation speeds, the curves are concave toward the rotation speed axis, indicating pseudoplastic behavior⁽²⁾. This pseudoplastic behavior becomes more pronounced at low temperature as the concentration of suspended crystals increases. We have analyzed the results in terms of an extended the power law indicated by Equation 3:

$$\log \tau_{yx} = A_1 + A_2 \log |du/dx| \quad 3)$$

where τ_{yx} is the shear stress and $|du/dx|$ the absolute value of the shear rate. The apparent viscosity, μ , is

$$\mu = \tau_{yx}/(du/dx) \quad 4)$$

The flow curve, Figure 2, is a plot of Equation 3 showing experimental results obtained at the 1185°C isotherm. Figure 3 is a log-log plot of apparent viscosity as a function of shear rate at the same temperature. The apparent viscosity decreases with increasing shear rate, which is characteristic for pseudoplastic systems⁽²⁾. The logarithm of the viscosity at unit shear rate, $\log \mu_0$, is calculated from Equation 3:

$$\log \mu_0 = A_1$$

5)

The results of least-squares analyses of \log (Viscosity) vs. reciprocal temperature are shown in Figure 4 and Table 3 for this investigation on Kilauea Iki basalt, the work of Shaw on Halemanumau basalt^(3,4) and Corey's report on Coal Slag X⁽⁵⁾. The Kilauea Iki data show a sharp increase in

Table 3. Apparent Activation Energies from Least Squares Analysis of \log (Viscosity) vs. $1/(T,K)$ for Kilauea Iki Basalt, Halemaumau Basalt^(3,4) and Coal Slag X⁽⁵⁾.

System	T, °C	Apparent Activation	Standard Deviation
		Energy, kcal mol ⁻¹	from Least Squares Fit
Kilauea Iki	1250-1170	138 ± 12	.11
	1170-1150	462 ± 28	.05
Halemaumau	1130-1158	86 ± 9	.12
	1158-1125	635 ± 64	.18
Coal Slag X	1482-1330	53 ± 1	.013
	1330-1260	424 ± 27	.14

slope at 1170°C as indicated by the limiting straight lines above and below this temperature. Below 1170°C, appreciable crystallization occurs as shown in Table 2 and Figure 1, and the system shows strongly pseudoplastic behavior. Shaw's⁽⁴⁾ results on Halemaumau basalt, which is a Hawaiian basalt quite similar to Kilauea Iki, show a sharp increase in slope at 1158°C. This system shows pseudoplastic behavior at 1125°C and Newtonian behavior at higher temperatures. The results of Corey⁽⁵⁾ on Coal Slag X indicate a sharp change in rheological behavior at 1330°C. His original paper gives no details on the calculation of the viscosity results, and no information on the crystallization sequence of the coal slag on which they were obtained. The similarity of the basalt and coal slag data may indicate that rheological behavior of the coal slag is also being affected by the presence of suspended crystalline material at temperatures near 1330°C. A recent study on slagging in large coal-burning furnaces correlates the slagging behavior with ash composition, ash particle morphology, and calculated critical viscosity temperature $T_{cv}^{(6)}$. The methods of the present investigation can be applied to measure the critical viscosity temperatures and compositions directly, which should improve the experimental basis for the correlation.

In both the studies on basalts, the breaks in the slope of the log (Viscosity)-reciprocal temperature curves occur at 20 to 30 volume percent of suspended crystals. The non-Newtonian behavior of these molten silicate suspensions appears to arise from the increasing concentration of suspended crystals in the melt. This suggests that in modeling fluid flow in silicate systems, power law behavior should be considered when the suspended crystal concentration exceeds 20 volume percent.

REFERENCES

- (1) Huebner, J. S. (1971) in Research Techniques for High Pressure and High Temperature, Ulmer, E. C. ed., Springer-Verlag, p. 146.
- (2) Skelland, A. H. P. (1967) Non-Newtonian Flow and Heat Transfer, Wiley, p. 5-12.
- (3) Shaw, H. R., Wright, T., Peck, D. L. and Okamura, R. (1968) Amer. Jour. Sci., Vol. 266, p. 225-264.
- (4) Shaw, H. R. (1969) Jour. Petrology, Vol. 10, p. 510-535.
- (5) Corey, Richard C. (1964), Bulletin No. 618, U.S. Bureau of Mines, P. 1-64.
- (6) Hazard, H.R. (1980) Influence of Coal Mineral Matter on Slagging of Utility Boilers, EPRI CS-1418, Project 736, Final Report, Electric Power Research Institute, Palo Alto, CA 94304.

This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory, under Contract No. W-7405-ENG-48.

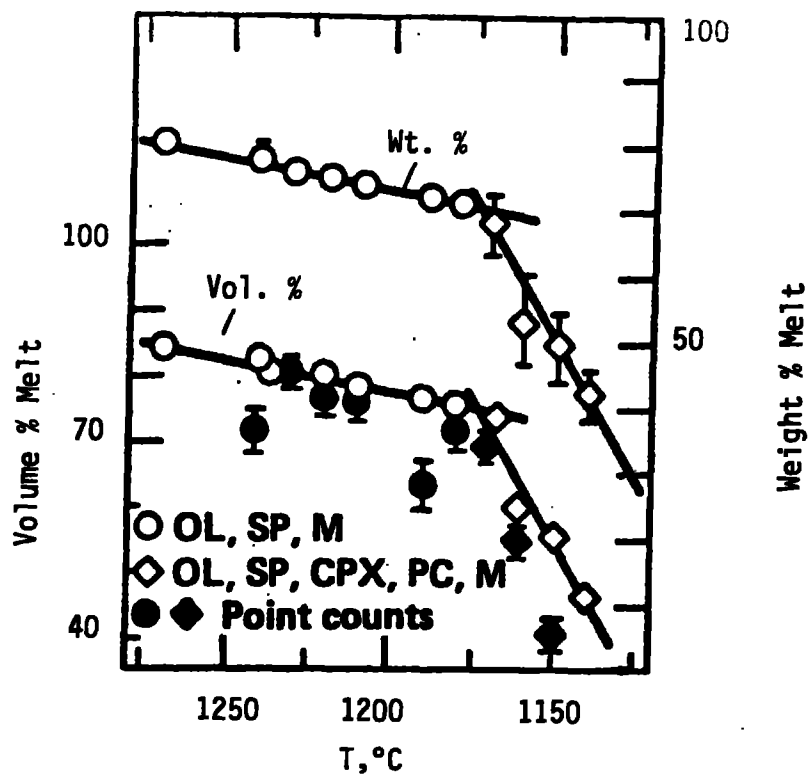


Fig. 1. Volume percent and weight percent melt as a function of temperature for Kilauea Iki basalt.

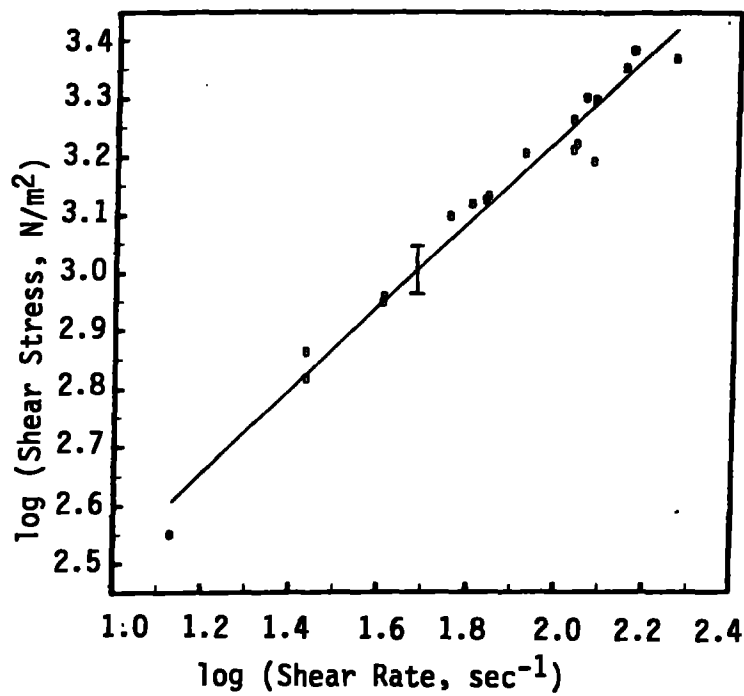


Fig. 2. Least-squares fit of \log (Shear Stress) vs. \log (Shear Rate) for Kilauea Iki basalt at 1185 $^{\circ}\text{C}$. Vertical bar indicates 2 standard deviations.

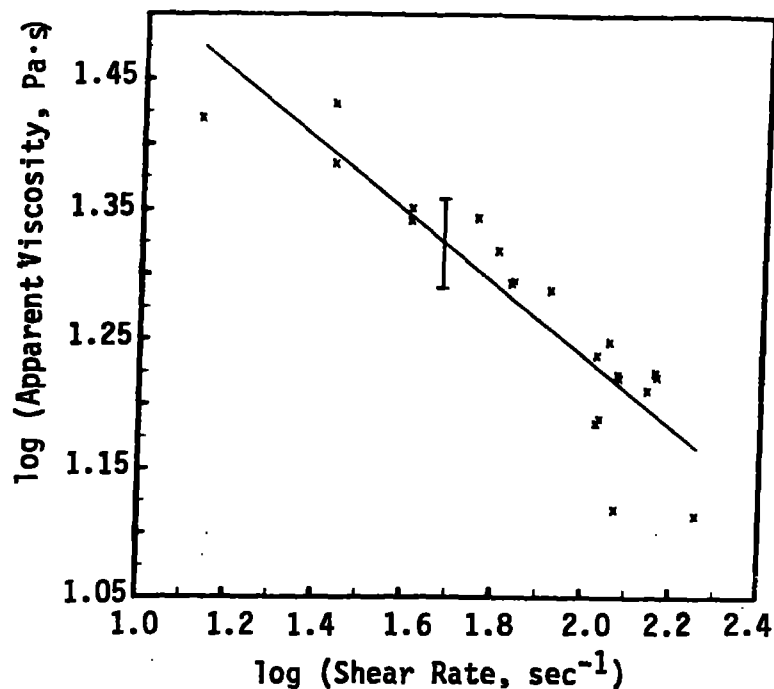


Fig. 3. Log (Apparent Viscosity) vs. log (Shear Rate) for Kilauea Iki basalt at 1185°C. Vertical bar indicates 2 standard deviations.

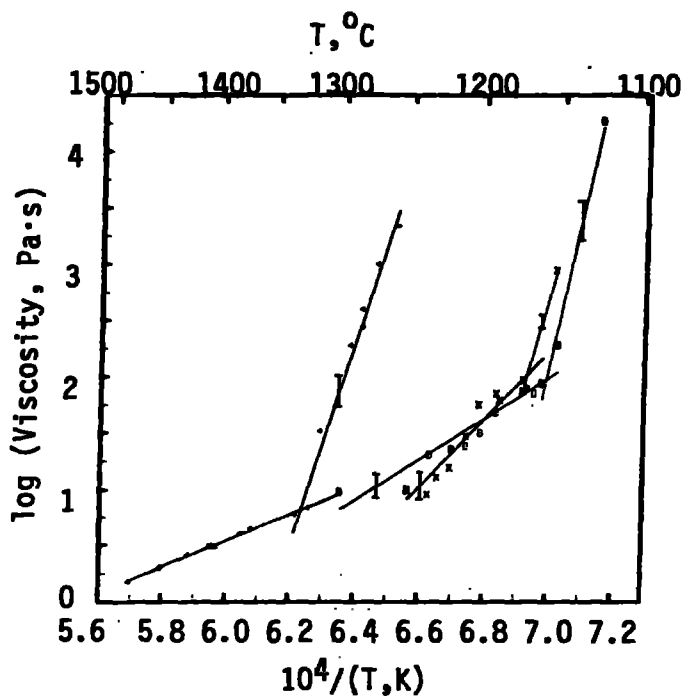


Fig. 4. Least squares analysis of log (Viscosity vs. reciprocal temperature. Present study, x; Shaw (1969) o; Corey (1962) +. Vertical bars indicate 2 standard deviations.